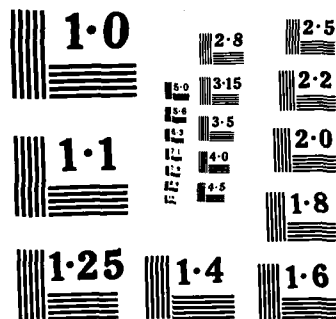


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The Detection and Study of Molecular Species  
Using Time Resolved Laser Spectroscopy

Final Report  
and  
Progress Report No. 4

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Yale University

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31 Dec. 1984

U.S. Army Research Office

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| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number)<br>New nsec and psec laser spectroscopic techniques are being developed for detect of specific molecular species. In the interest of general applicability, the efficiencies of the methods are being studied and improved by changing from nsec to psec excitation conditions. For specific applications to certain types of agents, we are studying photodecomposition as a method for producing a particular fragment characteristic of that agent-type and which can be detected with high sensitivity and specificity. |                              |   |

Final Report

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## 9. Brief Outline of Research Findings

The detection of trace compounds in the atmosphere and contaminants or other active agents in or on support facilities is of primary importance to the protection of military personnel. Two laser spectroscopic techniques have recently been developed which will provide considerable advantage in both sensitivity and selectivity; namely multiphoton ionization (MPI) spectroscopy and transient lensing (TL) spectroscopy. Multiphoton ionization spectroscopy has the ultimate sensitivity, being able to detect single atoms of material under the correct conditions. Transient lensing spectroscopy is much more sensitive than absorption spectroscopy, can be adapted for remote detection and is more general than fluorescence detection methods.

The purpose of this basic research effort is to study the underlying physical principles which control the efficiency of these methods with an eye to expanding their sensitivity and general applicability. The following report contains that work not covered in our previous reports.

Radiationless transitions to states with low ionization efficiency often severely limit the efficiency of multiphoton ionization. To study these processes directly and to investigate the effects of vibrational and rotational energy, we have obtained the energy analysis of the MPI photoelectrons in a photoelectron spectrometer. From these data we have found that, for the  $S_1$ -state of sym-triazine, the radiationless relaxation rates vary strongly with vibrational and rotational energy, ranging from  $10^7$  to  $> 10^{11}$  sec $^{-1}$ . This was determined by comparing the PES obtained with 10 nsec and 3 psec laser sources at a variety of wavelengths.

Our efforts to improve the efficiency of multiphoton ionization processes have also been particularly successful. We have found that by using ultraviolet radiation as an excitation source the overall efficiency can be dramatically improved. As a result, for instance, that  $O_2$ , which had not previously yielded an MPI excitation spectrum in spite of considerable effort by numerous groups, can be studied with relative ease. This approach has resulted in a wealth of new information on the electronic structure and photochemistry of  $O_2$ . We have observed 30 to 35 vibronic levels in the resonantly-enhanced MPI spectrum of a supersonic jet molecular beam of  $O_2$ , just in the laser wavelength region between 275 and 335 nm. All of these bands result from either two-photon or three-photon resonances. Nearly all of the states were previously unidentified. Many of the bands we have seen exhibit well defined rotational fine structure. This is most readily seen in spectra taken with moderate rotational cooling. Such moderate cooling minimizes the band overlap problem while leaving enough rotational structure for good analysis. This is illustrated for one band system (Figure 1) which has thereby been identified as a Rydberg state since the rotational and vibrational constants are very close to those of the ground state molecular ion. From its energy we know that this must be a two-photon transition to the lowest  $(3s\sigma) \ ^1\pi_g$  Rydberg state. This calls into question the earlier assignment of this state to features seen in the electron scattering data. The band in Figure 1 is clearly not one of those that were assigned to this  $^1\pi_g$  state in that work, and thus we anticipate a reevaluation of the electronic structure of  $O_2$ . Our results also show that many of the excited states in this energy region live considerably longer than believed previously.

I also made a second visit to the Ballistic Realistic Research Laboratory at the Aberdeen Proving Ground where I visited with Dr. R.A. Beyer and Dr. W.R. Anderson. We discussed several areas of common interest which I am considering as a portion of the continuation of this research effort. Of particular interest is the detection and study of radical fragments formed during the decomposition of high energy compounds. We have found that photodissociation processes re-

quiring numerous photons can be driven with high efficiency, producing large yields of atomic and small polyatomic fragments. These fragments can then be detected with high sensitivity, providing a laser-analytic method for atomic analysis of the precursor molecules. Multiphoton ionization coupled with MS and PES detection have been used to study the neutral products formed from both small and large polyatomic precursors. The dissociation pathway has been characterized in part by the energy state analysis of the products and from excitation spectra for the formation of particular products in specific states. In the case of sulfur dioxide for example, the yield of sulfur atoms is found to be affected via different states than those which result in the four photon ionization of the parent. Similarly, the rotational analysis of the bands observed in the MPI-MS spectra of methine and methylene are used to identify the electronic states and the rotational temperatures of the fragments formed from a variety of precursors.

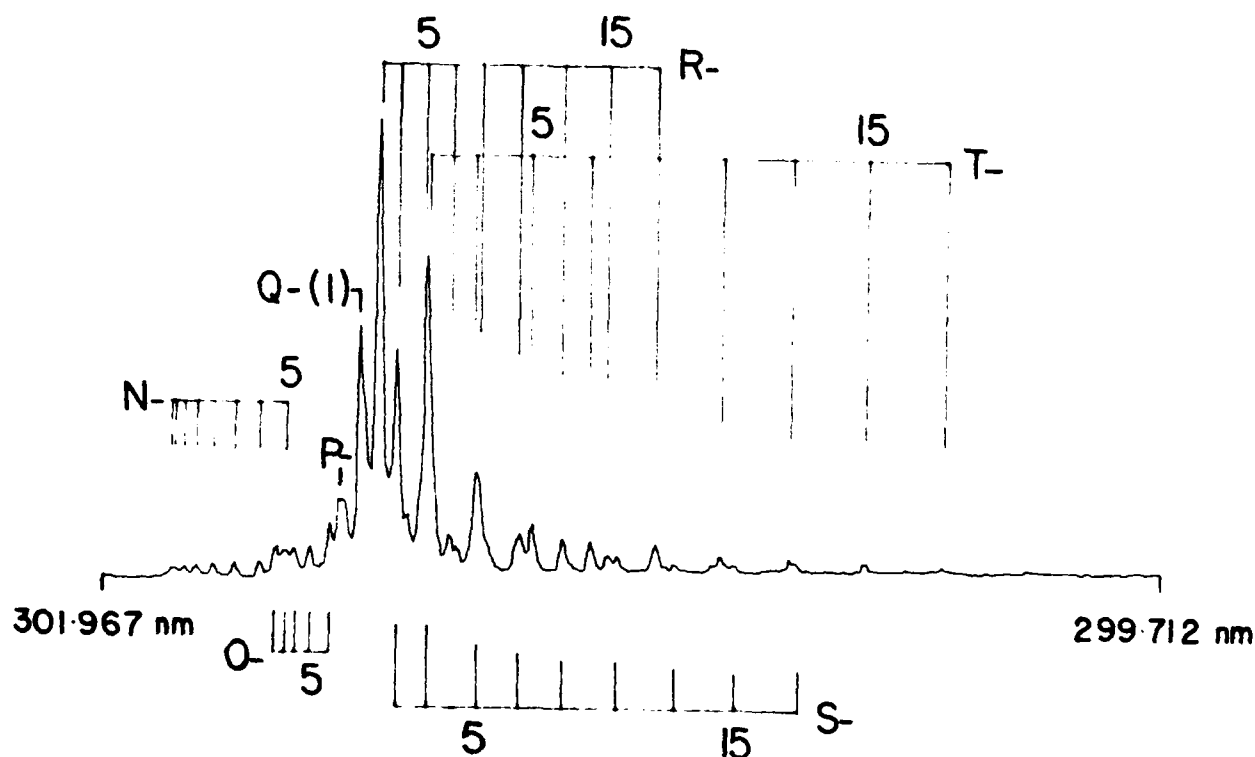


Figure Caption

- (1) Rotational Analysis of  $(3s\sigma)^1\Pi_g$  (0-0) band. Spectrum was taken in a supersonic expansion of neat  $O_2$ . Branch designations correspond to  $\Delta N = \pm 3, \pm 2, \pm 1, 0$ .

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